

# Preparation and Reactivity of Zirconium(III), Niobium(III), and Molybdenum(III) Complexes Stabilized by a Cyclopentadienyl Unit with Pendant Phosphine Donors

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This paper deals with the organometallic chemistry of the trivalent second-row transition metals of groups 4–6, namely, Zr, Nb, and Mo, with the cyclopentadienyldiphosphine ligand  $[\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{CH}_2\text{PR}_2)_2]$ , abbreviated as  $[\text{R}^2\text{P}_2\text{Cp}]$  (where R = *i*-Pr and Ph). The Zr(IV) complex  $[\text{i-Pr}^2\text{P}_2\text{Cp}]\text{ZrCl}_3$  undergoes reduction with Na/Hg to form the trivalent Zr derivative,  $[\text{i-Pr}^2\text{P}_2\text{Cp}]\text{ZrCl}_2$ , which undergoes a metathetical reaction with MeMgBr to yield the monomethyl derivative  $[\text{i-Pr}^2\text{P}_2\text{Cp}]\text{Zr}(\text{CH}_3)\text{Cl}$ . The reaction of the Zr(III) complex  $[\text{i-Pr}^2\text{P}_2\text{Cp}]\text{ZrCl}_2$  with excess carbon monoxide results in disproportionation to the Zr(IV) complex,  $[\text{i-Pr}^2\text{P}_2\text{Cp}]\text{ZrCl}_3$ , and the Zr(II) compound  $[\text{i-Pr}^2\text{P}_2\text{Cp}]\text{Zr}(\text{CO})_2\text{Cl}$ . This reaction is reversible, and upon removal of CO the starting material,  $[\text{i-Pr}^2\text{P}_2\text{Cp}]\text{ZrCl}_2$  is formed. The preparation of the diamagnetic Nb(III) complex  $[\text{R}^2\text{P}_2\text{Cp}]\text{NbCl}_2$  is achieved by the reaction of  $\text{NbCl}_3(\text{DME})$  with  $[\text{R}^2\text{P}_2\text{Cp}]\text{Li}$ .  $[\text{R}^2\text{P}_2\text{Cp}]\text{NbCl}_2$  complexes react with excess CO to form the CO adducts whose solid-state structures have been determined. The Nb(IV) derivatives  $[\text{R}^2\text{P}_2\text{Cp}]\text{NbCl}_3$  are formed via the reaction of  $[\text{R}^2\text{P}_2\text{Cp}]\text{NbCl}_2$  with  $\text{PbCl}_2$ . These complexes can also be produced when  $\text{Nb}(\text{O})\text{-Cl}_3(\text{THF})_2$  is allowed to react with excess  $[\text{R}^2\text{P}_2\text{Cp}]\text{Li}$ . These Nb(IV) derivatives are ESR active, and their solid-state molecular structures show distorted octahedral geometries around the Nb center.  $\text{MoCl}_3(\text{THF})_3$  reacts with  $[\text{R}^2\text{P}_2\text{Cp}]\text{Li}$  to generate the corresponding Mo(III) complexes  $[\text{R}^2\text{P}_2\text{Cp}]\text{MoCl}_2$ . These compounds are low-spin, paramagnetic complexes as evidenced by their ESR spectra.

## Introduction

Complexes that contain zirconium in the trivalent state are not particularly common.<sup>1</sup> Generally, one finds that attempts to prepare Zr(III) derivatives result in the formation of diamagnetic dinuclear species<sup>2–14</sup> unless sufficiently bulky ligands are utilized. For example, the

use of bulky cyclopentadienyl derivatives has allowed for the preparation of the mononuclear Zr(III) complexes  $(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}(\eta^8\text{-C}_8\text{H}_8)$ ,<sup>15</sup>  $(\eta^5\text{-1,3-C}_5\text{H}_3\text{Bu}^t_2)\text{ZrCl}$ ,<sup>16</sup> and  $\text{Bu}_4\text{N}\{[(\eta^5\text{-1,3-C}_5\text{H}_3(\text{SiMe}_3)_2)_2\text{ZrCl}_2]\}$ .<sup>14</sup> We recently reported<sup>17</sup> that mononuclear Zr(III) complexes could also be stabilized by the use of the bulky tridentate ligand  $\text{N}(\text{SiMe}_2\text{CH}_2\text{P}(\text{i-Pr})_2)_2$ . In these systems, complexes of the formula  $(\eta^5\text{-C}_5\text{H}_5)\text{ZrX}[\text{N}(\text{SiMe}_2\text{CH}_2\text{P}(\text{i-Pr})_2)_2]$  (X = Cl, H, or hydrocarbyl) could be isolated by virtue of the fact that the pendant phosphine arms can coordinate to the Zr(III) center and prevent dimerization.

A few years ago we reported the synthesis of a modified cyclopentadienyl ligand that contains pendant phosphine arms; the use of  $[\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{CH}_2\text{P}(\text{i-Pr})_2)_2]$ , abbreviated as  $[\text{i-Pr}^2\text{P}_2\text{Cp}]$ , allowed for the first structurally characterized zirconium alkylidene complex  $[\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{CH}_2\text{P}(\text{i-Pr})_2)_2]\text{Zr}=\text{CHPh}(\text{Cl})$ .<sup>18</sup> More recent work<sup>19</sup> with this ligand has shown that the presence of pendant phosphines attached to a cyclopentadienyl ligand generates systems that are fluxional due

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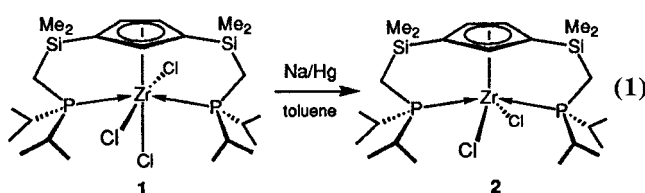
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to the fact that these pendant phosphine arms bind only weakly to Zr(IV). To fully assess the coordination chemistry of these modified cyclopentadienyl ligands, we have examined their ability to stabilize the relatively rare Zr(III) state. In addition, we also expanded this study to include groups 5 and 6 and report on the coordination chemistry of  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]$  ( $\text{R} = i\text{-Pr, Ph}$ ) with the related trivalent species Nb(III)<sup>20–26</sup> and Mo(III).<sup>27–30</sup>

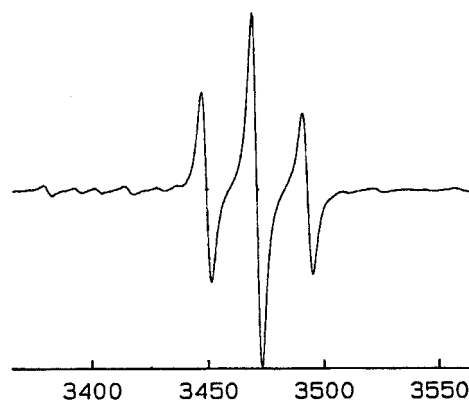
## Results and Discussion

**Synthesis and Reactivity of  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{Zr(III)}$  Complexes.** The reduction of the Zr(IV) precursor  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{ZrCl}_3$  (**1**)<sup>18</sup> with excess sodium amalgam (Na/Hg) in the absence of molecular nitrogen generates the Zr(III) complex  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{ZrCl}_2$  (**2**); during the reduction, the solution changes from a pale yellow to a dark green, which, after workup, leads to the isolation of dark green crystals of **2** (eq 1). If the reduction is performed under



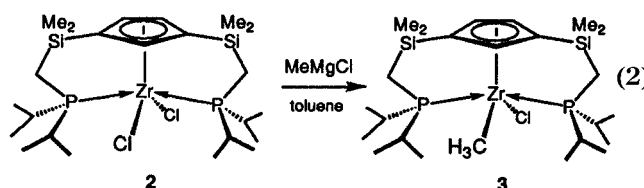
$\text{N}_2$ , the same green coloration is observed, but after a period of time, the green solution gradually turns deep brown due to the formation of a dinuclear dinitrogen complex.<sup>31</sup> The  $^1\text{H}$  NMR spectrum of **2** shows only broad resonances, and no signals are observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum; both observations are in agreement with the fact that the complex is paramagnetic. The ESR spectrum of **2** (Figure 1) shows a binomial triplet at  $g = 1.96$  with coupling to two  $^{31}\text{P}$  nuclei,  $a(^{31}\text{P}) = 22.7$  G, and satellites due to one magnetically dilute Zr nucleus,  $a(^{91}\text{Zr}) = 13.6$  G,  $^{91}\text{Zr} = 11.23\%$ ,  $I = 5/2$ . Magnetic measurements in solution by Evans' method<sup>32,33</sup> and the solid-state magnetic measurement give values of 1.8 and 2.0  $\mu_{\text{B}}$  for  $\mu_{\text{eff}}$ , respectively, corresponding to one unpaired electron. Mass spectrometry also confirms that **2** is mononuclear. Unfortunately, single crystals suitable for X-ray analysis could not be obtained.

Metathetical reactions of this complex have been examined. Complex **2** reacts with either 1 or 2 equiv of  $\text{CH}_3\text{MgCl}$  in toluene at  $-78$  °C (eq 2) to yield the



**Figure 1.** Room-temperature ESR spectrum of  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{ZrCl}_2$ , **2** (solution in toluene).

monomethyl derivative  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{Zr}(\text{CH}_3)\text{Cl}$  (**3**) as dark green microcrystals after workup. The elemental analy-



sis is consistent with the exchange of only one chloride of **2** for methyl in the product **3**. ESR spectroscopy shows a 10-line spectrum (Figure 2): a triplet of quartets centered at  $g = 2.01$ , due to coupling to two  $^{31}\text{P}$  nuclei,  $a(^{31}\text{P}) = 23.0$  G, the three methyl protons,  $a(^1\text{H}) = 8.0$  G, and satellites due to one  $^{91}\text{Zr}$  nucleus (not simulated). Unfortunately, despite many attempts, suitable crystals for X-ray analysis could not be obtained.

As already mentioned, even in the presence of 2 equiv of Grignard reagent, there is no evidence for the formation of any dimethyl derivative  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{Zr}(\text{CH}_3)_2$ , just monomethyl **3**. While we have no rationalization for this, we note that the related Zr(IV) precursor,  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{ZrCl}_3$  (**1**), can be converted quantitatively to the corresponding trimethyl,  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{Zr}(\text{CH}_3)_3$ , and other trialkyl derivatives.<sup>19,34</sup> Although dichloride **2** is consumed upon reaction with other alkylating agents such as  $\text{LiCH}_2\text{SiMe}_3$ ,  $\text{EtMgCl}$ , or  $\text{PhMgCl}$ , the isolation of pure materials was not possible. Apparently, for hydrocarbyl species bulkier than methyl groups, the reaction is not straightforward and decomposition to intractable materials occurs.

Treatment of a solution of **2** with carbon monoxide (1 atm, 25 °C) results in a rapid color change from dark green to deep brown. If the reaction is monitored by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, one observes the formation of two diamagnetic species; the ESR spectrum of this same sample showed only a very weak signal. On the basis of the NMR data, the solution contains a mixture of  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{Zr}(\text{CO})_2\text{Cl}$  (**4**) and  $[\text{R}^{\text{Pr}}\text{P}_2\text{Cp}]\text{ZrCl}_3$  (**1**); in other words, disproportionation of Zr(III) to Zr(II) and Zr(IV) has occurred. The resonances of trichloride **1** are easily assigned; what is also evident are two additional Cp resonances at 5.19 ppm (2H) and 5.21 ppm (1H) along with expected peaks for the  $\text{SiMe}_2\text{-CH}_2\text{P}$  portion of the pendant arms in the  $^1\text{H}$  NMR

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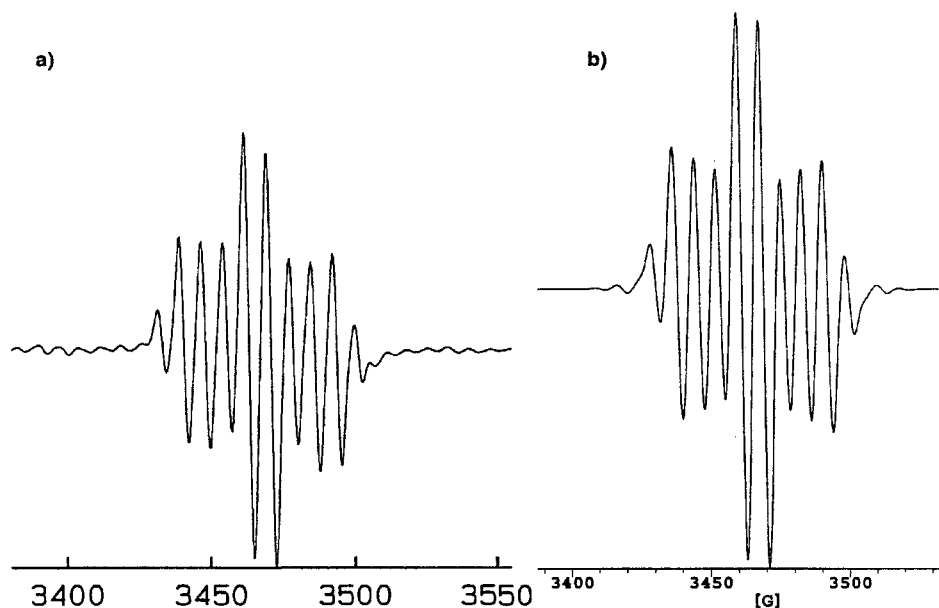
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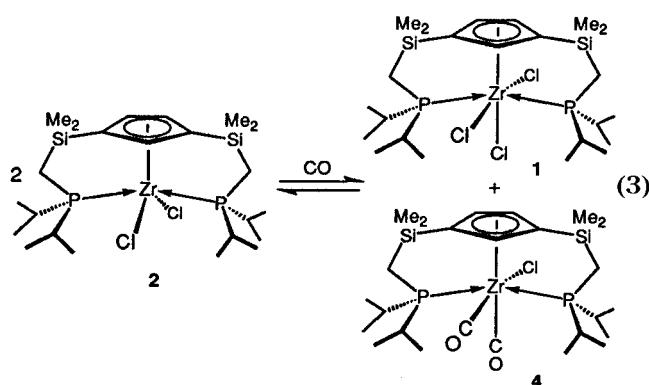
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**Figure 2.** (a) Room-temperature ESR spectrum of  $[i\text{-PrP}_2\text{Cp}]\text{Zr}(\text{CH}_3)\text{Cl}$ , **3** (solution in toluene). (b) Simulated spectrum (see Results and Discussion for details).

spectrum, and a sharp singlet at 31.6 ppm is observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The solution IR spectrum shows  $\bar{\nu}_{\text{CO}}$  stretches at 1888 and 1978  $\text{cm}^{-1}$ . The bromide derivative,  $[i\text{-PrP}_2\text{Cp}]\text{Zr}(\text{CO})_2\text{Br}$ , has been previously prepared,<sup>35</sup> and it displays very similar chemical shifts: 5.16 ppm (2H) and 5.19 ppm (1H) in the  $^1\text{H}$  NMR spectrum and 29.1 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. However, upon removal of the CO from the aforementioned reaction mixture, the color changed from dark brown to deep green, and the ESR and NMR spectra of the resulting product were identical to the paramagnetic dichloro derivative, **2**; this is summarized in eq 3. Such

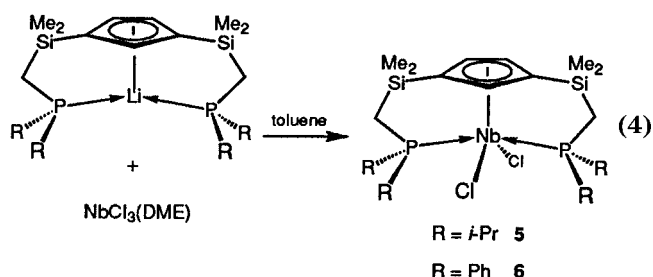


an equilibrium between Zr(III) and its disproportionation products does have precedent; for example, it has been shown that  $\text{CpZrCl}[\text{N}(\text{SiMe}_2\text{CH}_2\text{P}(i\text{-Pr})_2)_2]$  reacts with CO in a similar manner.<sup>36</sup>

To investigate the electronic and steric effects of the ligand on the stability and reactivity of the Zr(III) complexes, the synthesis of the corresponding Zr(IV) starting material  $[\text{PhP}_2\text{Cp}]\text{ZrCl}_3$  was attempted by the reaction of  $[\text{PhP}_2\text{Cp}]\text{Li}$  with  $\text{ZrCl}_4(\text{THT})_2$ . However, no reaction was observed even after prolonged reaction times and with heating to 65  $^\circ\text{C}$ ; only starting materials

were isolated. Presumably, the phenyl groups attached to phosphorus in the  $[\text{PhP}_2\text{Cp}]$  ligand are more electron withdrawing than the *i*-Pr groups of the corresponding derivative  $[i\text{-PrP}_2\text{Cp}]$ , and this combined with the fact that Zr(IV) is an electron-poor,  $d^0$  metal center renders this combination ineffective.

**Synthesis and Reactivity of  $[\text{R}^i\text{P}_2\text{Cp}]\text{Nb}(\text{III})$  Complexes.** When  $\text{NbCl}_3(\text{DME})$  is allowed to react with  $[\text{R}^i\text{P}_2\text{Cp}]\text{Li}$  at room temperature in toluene, the initial brown color of the solution changes to brown-red after 4 h. Upon workup of the reaction mixture, one obtains cherry-red, microcrystalline solids in good yield, which are formulated as  $[\text{R}^i\text{P}_2\text{Cp}]\text{NbCl}_2$  (**5**,  $\text{R} = i\text{-Pr}$ ; **6**,  $\text{R} = \text{Ph}$ ) (eq 4) according to the elemental analysis.  $^1\text{H}$  NMR



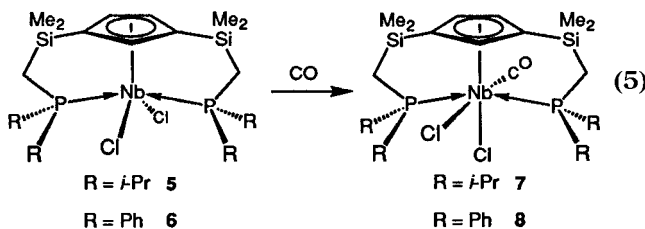
studies show that **5** and **6** are diamagnetic complexes with the Cp resonances at 4.70 ppm (1H) and 5.60 ppm (2H) for **5** and 5.25 ppm (2H) and 5.5 ppm (1H) for **6**.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy shows quadrupolar-broadened singlets at 24.6 ppm for **5** and 22.5 ppm for **6** ( $^{93}\text{Nb}$ ,  $I = 9/2$ , 100%). Mass spectrometry and molecular weight determinations indicate that **5** and **6** are mononuclear. The 16-electron monocyclopentadienyl Nb(III) compounds reported in the literature either are paramagnetic, such as  $(\eta^5\text{-C}_5\text{Me}_5)\text{NbCl}_2(\text{PMe}_3)_2$ ,<sup>21</sup> or show contact-shifted NMR signals, such as  $(\eta^5\text{-C}_5\text{Me}_5)\text{NbCl}_2(\text{PMe}_2\text{Ph})_2$  and  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{NbCl}_2(\text{PEt}_3)_2$ .<sup>20</sup> The only example of a diamagnetic species of this type is the complex  $(\eta^5\text{-C}_5\text{H}_5)\text{NbCl}_2(\text{dppe})$ .<sup>20</sup> There are of course diamagnetic Nb(III) dimers with Nb–Nb bonds such as

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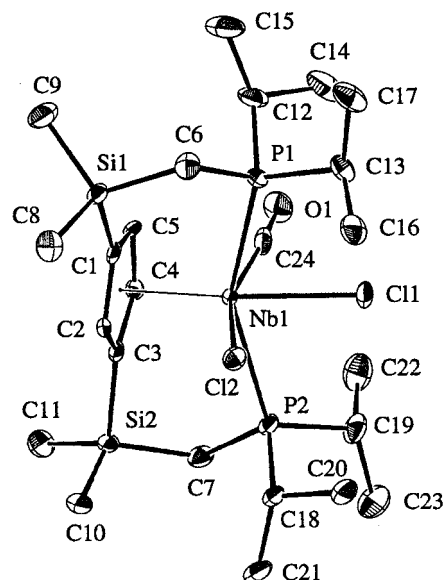
{ $(\eta^5\text{-C}_5\text{Me}_5)\text{NbCl}_2$ }.<sup>23</sup> Although **5** and **6** can be crystallized from toluene, the crystals obtained were not suitable for X-ray analysis.

When **5** and **6** are dissolved in toluene and placed under 1 atm of CO, the color of the solution changes from dark red to orange and microcrystalline solids can be isolated. Elemental analysis identifies the compounds as  $[\text{R}^i\text{P}_2\text{Cp}]\text{Nb}(\text{CO})\text{Cl}_2$  (**7**, R = *i*-Pr; **8**, R = Ph; eq 5). Both

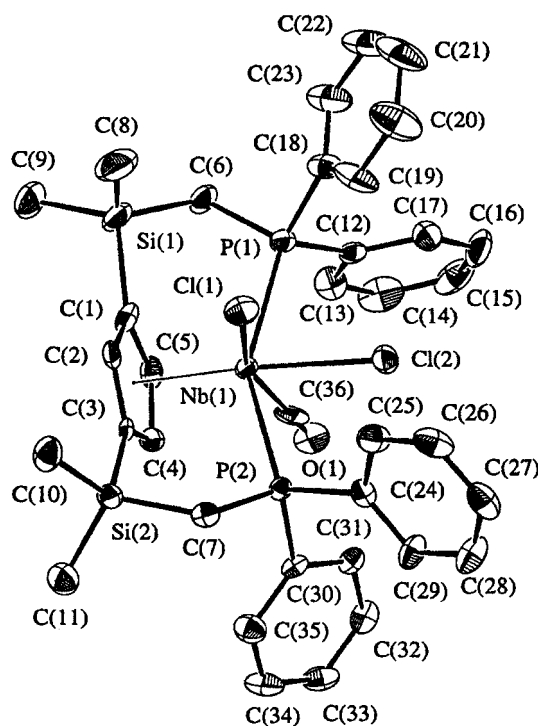


are 18-electron complexes with the  $\bar{\nu}_{\text{CO}}$  stretching vibration at  $1914\text{ cm}^{-1}$  for **7** and  $1927\text{ cm}^{-1}$  for **8**, typical for Nb(III) derivatives.<sup>21,22,37,38</sup> Compounds **7** and **8** are diamagnetic, with  $^1\text{H}$  NMR resonances for the unique Cp at 4.4 ppm (2H) and 6.0 ppm (1H) for **7** and 4.5 ppm (2H) and 6.4 ppm (1H) for **8**. The chemical shifts for the resonances due to the silylmethyls and the methylene protons of the ligand are very similar in both compounds.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra show quadrupolar-broadened singlets at 25.85 ppm for **7** and 18.20 ppm for **8**. All mononuclear carbonyl derivatives of  $(\eta^5\text{-C}_5\text{H}_5)\text{-NbCl}_2\text{L}_2$  described in the literature are also diamagnetic.<sup>21,23-26,37-39</sup> One curious point is that the monocarbonyl complexes are all formed stereoselectively, with the carbonyl ligand bound on the side opposite the unique carbon of the cyclopentadienyl unit. In solution, no isomers are detected, and the stereochemistry of the final products **7** and **8** is evident from the crystal structures described below.

Crystals suitable for X-ray analysis were grown from toluene. The crystal structures of **7** and **8** are shown in Figures 3 and 4, respectively. Both show pseudo-octahedral arrangements, fairly common in monocyclopentadienyl Nb(III) 18-electron complexes, where CO, Cl, and both phosphines occupy pseudoequatorial positions and the Cp ring and the other Cl atom occupying the apical positions. The Nb atom in each complex is not found in the equatorial plane, but is located approximately 0.61 Å above it. The Nb–C (CO) bond (2.0823(3) Å) is shorter in **7** than in **8** (2.138(4) Å), and consequently the C–O bond length (1.149(4) Å) in **7** is longer than in **8** (1.044(4) Å). This is not surprising, because the phosphine substituents in **7** are more electron-releasing (*i*-Pr) than those in **8** (Ph). The additional electron density in **7** results in increased M–C–O  $\pi$ -back-bonding, thus resulting in stronger M–C and weaker C–O bonds. This is consistent with the observed CO stretching frequencies for both complexes. Both Nb–P bond distances are identical (within experimental error) in **8**, but in **7** one is 0.013 Å longer than the other. The Nb–Cl (axial) bond distances are similar in both structures, but the Nb–Cl (equatorial)



**Figure 3.** Molecular structure and numbering scheme of  $[\textit{i}\text{-Pr}_2\text{P}_2\text{Cp}]\text{Nb}(\text{CO})\text{Cl}_2$ , **7**.



**Figure 4.** Molecular representation and numbering scheme of  $[\text{Ph}_2\text{P}_2\text{Cp}]\text{Nb}(\text{CO})\text{Cl}_2$ , **8**.

**Table 1: Selected Bond Lengths in  $[\textit{i}\text{-Pr}_2\text{P}_2\text{Cp}]\text{NbCl}_2(\text{CO})$ , **7****

| atom | atom  | distance (Å) | atom  | atom  | distance (Å) |
|------|-------|--------------|-------|-------|--------------|
| Nb   | Cl(1) | 2.5021(8)    | Nb    | C(3)  | 2.483(3)     |
| Nb   | Cl(2) | 2.5867(7)    | Nb    | C(4)  | 2.384(3)     |
| Nb   | P(1)  | 2.7020(8)    | Nb    | C(5)  | 2.330(3)     |
| Nb   | P(2)  | 2.7150(9)    | Nb    | Cp    | 2.081        |
| Nb   | C(1)  | 2.382(3)     | Nb    | C(24) | 2.082(3)     |
| Nb   | C(2)  | 2.458(3)     | C(24) | O(1)  | 1.149(4)     |

bond lengths are different because the chlorides are trans to CO and are affected by variations in M–C (CO) bond lengths. Selected bond lengths and bond angles are collected in Tables 1–4.

Attempts to introduce alkyl groups at niobium via the reaction with Grignard reagents were examined with

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**Table 2: Selected Bond Angles in  $[i\text{-Pr}_2\text{P}_2\text{Cp}]_2\text{NbCl}_2(\text{CO})$ , **7****

| atom  | atom | atom  | angle (deg) | atom  | atom | atom  | angle (deg) |
|-------|------|-------|-------------|-------|------|-------|-------------|
| Cl(1) | Nb   | Cl(2) | 85.29(3)    | P(2)  | Nb   | C(24) | 92.61(9)    |
| P(1)  | Nb   | P(2)  | 152.45(3)   | Cl(1) | Nb   | Cp    | 171.1       |
| Cl(1) | Nb   | P(1)  | 76.49(3)    | Cl(2) | Nb   | Cp    | 103.6       |
| Cl(2) | Nb   | P(2)  | 86.98(2)    | P(1)  | Nb   | Cp    | 103.9       |
| Cl(1) | Nb   | C(24) | 75.54(9)    | P(2)  | Nb   | Cp    | 103.5       |
| Cl(2) | Nb   | C(24) | 160.39(9)   | C(24) | Nb   | Cp    | 95.6        |
| P(1)  | Nb   | C(24) | 88.21(9)    |       |      |       |             |

**Table 3: Selected Bond Lengths in  $[\text{Ph}_2\text{P}_2\text{Cp}]_2\text{NbCl}_2(\text{CO})$ , **8****

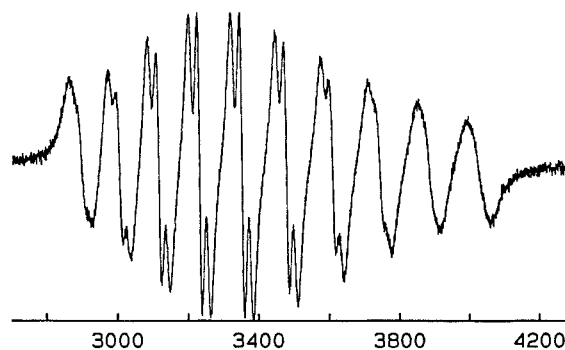
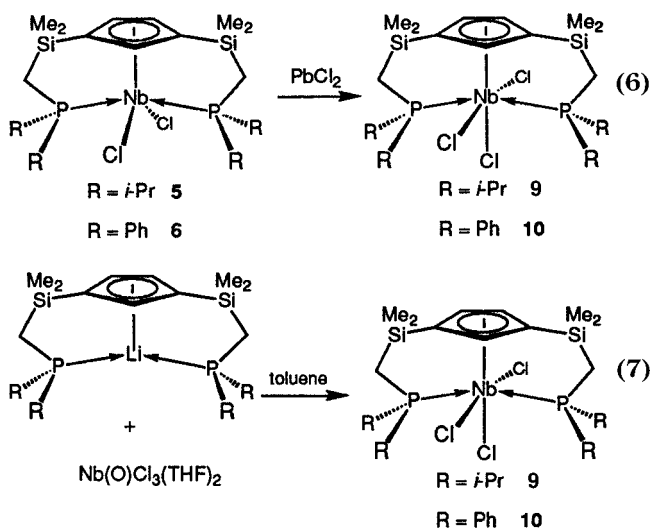
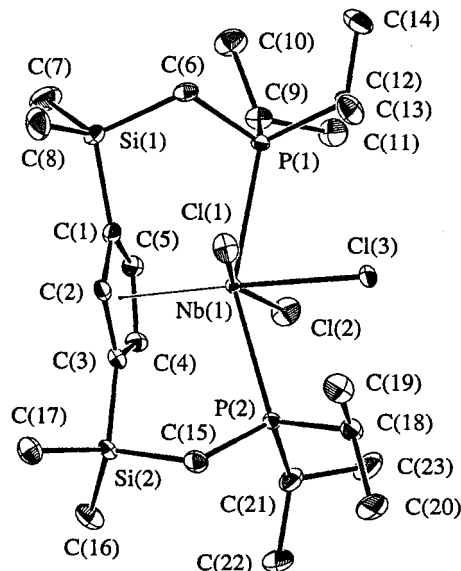
| atom | atom  | distance (Å) | atom  | atom  | distance (Å) |
|------|-------|--------------|-------|-------|--------------|
| Nb   | Cl(1) | 2.5724(9)    | Nb    | C(3)  | 2.458(3)     |
| Nb   | Cl(2) | 2.4927(10)   | Nb    | C(4)  | 2.364(3)     |
| Nb   | P(1)  | 2.6822(10)   | Nb    | C(5)  | 2.353(3)     |
| Nb   | P(2)  | 2.6849(9)    | Nb    | Cp    | 2.090        |
| Nb   | C(1)  | 2.436(4)     | Nb    | C(36) | 2.138(4)     |
| Nb   | C(2)  | 2.462(3)     | C(36) | O(1)  | 1.049(4)     |

**Table 4: Selected Bond Angles in  $[\text{Ph}_2\text{P}_2\text{Cp}]_2\text{NbCl}_2(\text{CO})$ , **8****

| atom  | atom | atom  | angle (deg) | atom  | atom | atom  | angle (deg) |
|-------|------|-------|-------------|-------|------|-------|-------------|
| Cl(1) | Nb   | Cl(2) | 85.83(3)    | P(2)  | Nb   | C(36) | 89.32(9)    |
| P(1)  | Nb   | P(2)  | 152.73(3)   | Cl(1) | Nb   | Cp    | 103.4       |
| Cl(1) | Nb   | P(1)  | 92.83(3)    | Cl(2) | Nb   | Cp    | 170.8       |
| Cl(2) | Nb   | P(2)  | 77.48(3)    | P(1)  | Nb   | Cp    | 104.2       |
| Cl(1) | Nb   | C(36) | 159.77(11)  | P(2)  | Nb   | Cp    | 102.9       |
| Cl(2) | Nb   | C(36) | 74.10(11)   | C(36) | Nb   | Cp    | 96.7        |
| P(1)  | Nb   | C(36) | 84.62(9)    |       |      |       |             |

both Nb(III) compounds. When **5** was allowed to react with 2 equiv of MeMgBr, only mixtures of products were obtained; a similar result was observed with **6**. The NMR spectra of the crude material indicated that the product consisted of a mixture of two compounds. All attempts to separate these two complexes have failed due to their similar solubilities in common solvents. In the absence of strong evidence, we can only speculate that these species are the mono- and dimethyl derivatives,  $[\text{R}_2\text{P}_2\text{Cp}]_2\text{NbMe}_2$  ( $X = \text{Cl}$  or  $\text{Br}$ ) and  $[\text{R}_2\text{P}_2\text{Cp}]_2\text{NbMe}_2$ . Both **5** and **6** react with  $\text{LiCH}_2\text{SiMe}_3$  to produce brown oils that are mixtures of two compounds based on their NMR spectra; presumably, these mixtures are also mono- and dialkylated derivatives.

Oxidation of the Nb(III) derivatives  $[\text{R}_2\text{P}_2\text{Cp}]_2\text{NbCl}_2$  with  $\text{PbCl}_2$  results in the formation of the niobium(IV) complexes  $[\text{R}_2\text{P}_2\text{Cp}]_2\text{NbCl}_3$  (**9**,  $R = i\text{-Pr}$ ; **10**,  $R = \text{Ph}$ );

**Figure 5.** Room-temperature ESR spectrum of  $[i\text{-Pr}_2\text{P}_2\text{Cp}]_2\text{NbCl}_3$ , **9** (solution in toluene).**Figure 6.** Molecular structure and numbering scheme of  $[i\text{-Pr}_2\text{P}_2\text{Cp}]_2\text{NbCl}_3$ , **9**.

although this process is difficult to control and overoxidation complicates isolation of the Nb(IV) derivatives, ESR spectroscopy clearly shows that the Nb(IV) species are formed (eq 7). For **9**, a decet of triplets centered at  $g = 2.035$  is observed, while for **10** this pattern is found at  $g = 2.036$ . The unpaired electron on each Nb(IV) center is coupled to two equivalent phosphines,  $a(^{31}\text{P}) = 26$  and  $21$  G, and one Nb atom,  $a(^{93}\text{Nb}) = 124$  and  $117$  G ( $^{93}\text{Nb}$ ,  $I = 9/2$ , 100%), for **9** and **10**, respectively. The ESR spectrum of **9** is shown in Figure 5. The same complexes are produced when  $\text{NbCl}_3(\text{O})(\text{THF})_2$  reacts with  $[\text{R}_2\text{P}_2\text{Cp}]\text{Li}$  (eq 7). The yield of this latter reaction is 45% and 37% for **9** and **10**, respectively. This reaction was performed originally to synthesize Nb(V) derivatives of the  $[\text{R}_2\text{P}_2\text{Cp}]$  ligand, but the dark green color of the reaction mixture, the ESR spectrum, and the X-ray analysis of **9**, all attest to the formation of **9** and **10**. The mechanism for the reaction in eq 7 is not obvious. Since a reduction from Nb(V) to Nb(IV) is observed, one possible rationale is that the reducing agent is the phosphine ligand (used in excess); unfortunately, no corroborating evidence was obtained.

The crystal structure of **9** is shown in Figure 6 and indicates a pseudo-octahedral geometry around the metal center. Assuming that the Cp ring occupies only one site, two chlorides and both phosphines form a pseudoequatorial plane, while the Cp ring and the third Cl occupy the apical positions. The molecule is distorted

**Table 5: Selected Bond Lengths in  $[i\text{-Pr}]\text{P}_2\text{Cp}]\text{NbCl}_3$ , **9****

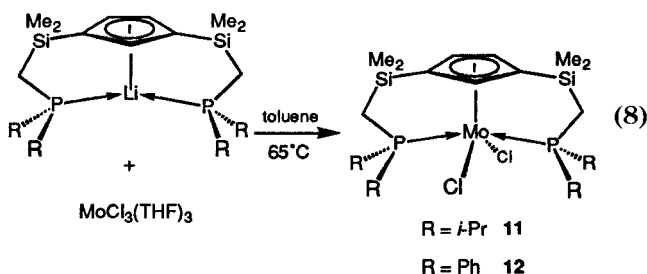
| atom | atom  | distance (Å) | atom | atom | distance (Å) |
|------|-------|--------------|------|------|--------------|
| Nb   | Cl(1) | 2.5121(6)    | Nb   | C(2) | 2.481(3)     |
| Nb   | Cl(2) | 2.5284(7)    | Nb   | C(3) | 2.503(3)     |
| Nb   | Cl(3) | 2.4771(7)    | Nb   | C(4) | 2.414(3)     |
| Nb   | P(1)  | 2.7365(6)    | Nb   | C(5) | 2.391(3)     |
| Nb   | P(2)  | 2.7194(6)    | Nb   | Cp   | 2.13         |
| Nb   | C(1)  | 2.442(3)     |      |      |              |

**Table 6: Selected Bond Angles in  $[i\text{-Pr}]\text{P}_2\text{Cp}]\text{NbCl}_3$ , **9****

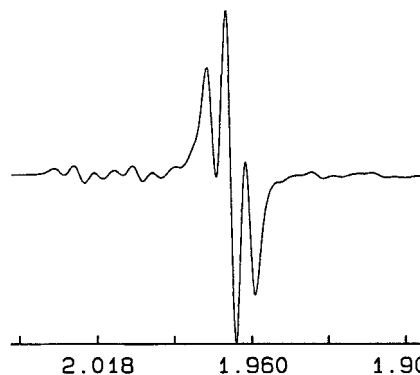
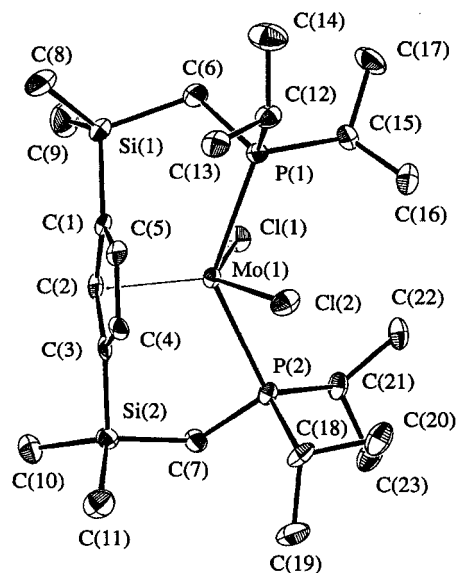
| atom  | atom | atom  | angle (deg) | atom  | atom | atom | angle (deg) |
|-------|------|-------|-------------|-------|------|------|-------------|
| Cl(1) | Nb   | Cl(2) | 160.53(3)   | Cl(3) | Nb   | P(2) | 75.93(2)    |
| Cl(1) | Nb   | Cl(3) | 83.03(2)    | Cl(1) | Nb   | Cp   | 100.3       |
| Cl(2) | Nb   | Cl(3) | 77.87(3)    | Cl(2) | Nb   | Cp   | 98.9        |
| Cl(1) | Nb   | P(1)  | 83.62(2)    | Cl(3) | Nb   | Cp   | 176.5       |
| Cl(1) | Nb   | P(2)  | 88.23(2)    | P(1)  | Nb   | P(2) | 152.98(2)   |
| Cl(2) | Nb   | P(1)  | 90.73(2)    | P(1)  | Nb   | Cp   | 103.8       |
| Cl(2) | Nb   | P(2)  | 90.73(2)    | P(2)  | Nb   | Cp   | 103.0       |
| Cl(3) | Nb   | P(1)  | 77.53(2)    |       |      |      |             |

because both Cl(1)–Nb–Cl(2) (160.53(3)°) and P(1)–Nb–P(2) (152.98(3)°) angles depart by 20° and 30° from 180°. The Nb atom lies 0.5391 Å above the equatorial plane toward the Cp ring. Nb–Cl (equatorial) and Nb–P bond lengths are longer than those found in CpNbCl<sub>3</sub>-dppe.<sup>40,41</sup> The structure compares very well with the structure of the zirconium(IV) analogue,  $[i\text{-Pr}]\text{P}_2\text{Cp}]\text{ZrCl}_3$  (**1**), which has a similar geometry and comparable bond lengths and angles.<sup>19</sup> Selected bond lengths and bond angles are shown in Tables 5 and 6.

**Synthesis and Reactivity of  $[\text{R}]\text{P}_2\text{Cp}]\text{Mo(III)}$  Complexes.** MoCl<sub>3</sub>(THF)<sub>3</sub> reacts with  $[\text{R}]\text{P}_2\text{Cp}]\text{Li}$  in toluene at 65 °C to form brown solutions, which upon workup yield brown microcrystalline solids (eq 8). These compounds have the molecular formula  $[\text{R}]\text{P}_2\text{Cp}]\text{MoCl}_2$  (**11**, R = *i*-Pr; **12**, R = Ph).



Solutions of **11** and **12** show broad, unresolved signals in their respective NMR spectra; both solution magnetic studies by the Evans' method and magnetic susceptibility measurements on solid samples show that the effective magnetic moments 1.98 and 2.10  $\mu_B$  are consistent with one unpaired electron on **11** and **12**, respectively. Magnetic studies for low-spin Mo(III) complexes are rare, because most pseudo-octahedral Mo(III) compounds have high-spin ( $S = 3/2$ ) electronic ground states.<sup>27</sup> The effective magnetic moment for the closely related compound  $(\eta^5\text{-C}_5\text{H}_5)\text{MoCl}_2(\text{PMe}_3)_2$  is 1.72  $\mu_B$ .<sup>27</sup> Room-temperature solution ESR spectra of **11** and **12** in toluene are observed as broad triplets at  $g = 1.97$  and 1.98, respectively, due to coupling to two equivalent phosphorus nuclei ( $a(^{31}\text{P}) = 15.2$  G for **11** and 11.0 G

**Figure 7.** Room-temperature ESR spectrum of  $[i\text{-Pr}]\text{P}_2\text{Cp}]\text{MoCl}_2$ , **11** (solution in toluene).**Figure 8.** Molecular structure and numbering scheme of  $[i\text{-Pr}]\text{P}_2\text{Cp}]\text{MoCl}_2$ , **11**.

for **12**) and satellites due to one magnetically dilute Mo nucleus ( $a(^{95,97}\text{Mo}) = 39.1$  G for **11** and 43.4 G for **12**:  $^{95}\text{Mo}$  and  $^{97}\text{Mo}$ , 25% total,  $I = 5/2$ ). The ESR spectrum for **11** is shown in Figure 7. Since most Mo(III) complexes are in a  $S = 3/2$  spin state, they show unresolved singlets in their room-temperature ESR spectra. There are some examples of low-spin Mo(III) complexes that show well-resolved ESR spectra with hyperfine couplings; for example,  $(\eta^5\text{-C}_5\text{H}_5)\text{MoCl}_2(\text{PMe}_3)_2$  and  $(\eta^5\text{-C}_5\text{H}_5)\text{MoX}_2(\text{dppe})$ , X = halide, have  $g$  values of about 1.98.<sup>27</sup>

The crystal structure of **11** is shown in Figure 8. A comparison of the bond angles around the Mo center suggests that the coordination environment can be described as a distorted square pyramid with the phosphine donor atoms and both chlorides in the same plane, which is capped by the Cp ring. The Mo atom lies 0.9465 Å above the Cl<sub>2</sub>P<sub>2</sub> plane toward the Cp ring. The geometry of the molecule can be referred to as a "four-legged piano stool". The Mo–C (Cp) distances (average 2.301 Å) are slightly longer than those of  $(\eta^5\text{-C}_5\text{H}_5)\text{MoCl}_2(\text{PMe}_3)_2$  (2.272 Å), but Mo–Cl distances are very similar (average 2.479 Å vs 2.471 Å).<sup>27</sup> The lengthening of the Mo–P bond distances in **11** (average Mo–P bond distance 2.5645(7) Å) as compared to those in  $(\eta^5\text{-C}_5\text{H}_5)\text{MoCl}_2(\text{PMe}_3)_2$  (2.482(2) Å)<sup>27</sup> is probably caused by the steric bulk of the  $[\text{P}_2\text{Cp}]$  ligand that

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**Table 7: Selected Bond Lengths in [<sup>i</sup>-PrP<sub>2</sub>Cp]MoCl<sub>2</sub>, 11**

| atom | atom  | distance (Å) | atom | atom | distance (Å) |
|------|-------|--------------|------|------|--------------|
| Mo   | Cl(1) | 2.4899(8)    | Mo   | C(2) | 2.339(3)     |
| Mo   | Cl(2) | 2.4678(8)    | Mo   | C(3) | 2.395(3)     |
| Mo   | P(1)  | 2.5380(7)    | Mo   | C(4) | 2.301(3)     |
| Mo   | P(2)  | 2.5910(8)    | Mo   | C(5) | 2.216(3)     |
| Mo   | C(1)  | 2.254(3)     | Mo   | Cp   | 1.955        |

**Table 8: Selected Bond Angles in [<sup>i</sup>-PrP<sub>2</sub>Cp]MoCl<sub>2</sub>, 11**

| atom  | atom | atom  | angle (deg) | atom  | atom | atom | angle (deg) |
|-------|------|-------|-------------|-------|------|------|-------------|
| Cl(1) | Mo   | Cl(2) | 135.40(3)   | Cl(1) | Mo   | Cp   | 110.3       |
| P(1)  | Mo   | P(2)  | 136.28(3)   | Cl(2) | Mo   | Cp   | 114.3       |
| Cl(1) | Mo   | P(1)  | 79.75(3)    | P(1)  | Mo   | Cp   | 113.0       |
| Cl(2) | Mo   | P(2)  | 84.20(3)    | P(2)  | Mo   | Cp   | 110.5       |

pushes the phosphines slightly away from the Mo(III) center, since the electronic factors in these two compounds are very similar; confirmation of this is apparent from the longer Mo–P bond distances in ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>-MoCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>) of 2.5104(8) and 2.5080(8) Å.<sup>42</sup> An examination of C–C bond distances of the Cp ring and Mo–C(Cp) bond lengths shows that the bonding of Cp to the metal is consistent with  $\eta^2, \eta^3$  character. The carbons of the  $\eta^3$  system, C(2), C(3), and C(4), are further away from the metal than C(1) and C(5), which belong to the  $\eta^2$  system. In many piano-stool complexes a slight tilting of the Cp ring from a plane perpendicular to the Cp–M axis is observed.<sup>27</sup> Selected bond lengths and bond angles are show in Tables 7 and 8.

Complex 11 reacts with MeMgBr at –78 °C, to yield a brown oil, which shows a broad singlet in its ESR spectrum. The product is NMR active, and both <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra indicate that the crude product is a mixture of compounds. All attempts to separate and characterize these species have proved futile.

### Conclusions

The use of a cyclopentadienyl ligand with pendant donors is not a new approach to ligand design. Indeed, there are many examples of this in the literature.<sup>43,44</sup> What is significant about this work is that the examples of complexes of the general type CpMCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> have been prepared for M = Zr, Nb, and Mo with a modified cyclopentadienyl with two pendant phosphine donors. Other cyclopentadienyl units with one pendant phosphine are known.<sup>43,45–47</sup> However, our approach to using two pendant phosphine donors is unique to our knowledge. These complexes are reactive, as evidenced by their reactivity with carbon monoxide. Attempts to generate alkyl derivatives of these second-row trivalent metal complexes have only been partially successful. In general complicated mixtures result that have so far eluded purification.

### Experimental Section

**General Procedures.** Unless otherwise stated all manipulations were carried out under an atmosphere of dry, oxygen-

free dinitrogen or argon by means of standard Schlenk or glovebox techniques.<sup>48</sup> Hexanes, toluene, Et<sub>2</sub>O, and THF were refluxed over CaH prior to a final distillation from either sodium metal or sodium benzophenone ketyl under an Ar atmosphere. Deuterated solvents were dried over potassium and vacuum transferred. They were then degassed by three “freeze–pump–thaw” cycles. The solid-state magnetic measurements were determined from Gouy measurements performed on a Johnson Matthey MSB-1 apparatus at room temperature. The magnetic measurements in solution were performed using Evans’ method with ferrocene as standard.<sup>32,33</sup>

**Reagent Syntheses.** 1,1-C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>CH<sub>2</sub>Cl)<sub>2</sub>,<sup>34</sup> [<sup>i</sup>-PrP<sub>2</sub>Cp]-ZrCl<sub>3</sub>,<sup>19</sup> [<sup>i</sup>-PrP<sub>2</sub>Cp]Li,<sup>18</sup> NbCl<sub>3</sub>(DME),<sup>49</sup> Nb(O)Cl<sub>3</sub>(THF)<sub>2</sub>,<sup>50</sup> and MoCl<sub>3</sub>(THF)<sub>3</sub><sup>51</sup> were prepared using literature procedures. Mercury was purchased from BDH and purified following a literature procedure.<sup>52</sup> Sodium amalgam was made under a nitrogen atmosphere and washed with toluene until the washing showed no gray coloration. MeMgCl and MeMgBr (3 M solutions in diethyl ether) were purchased from Aldrich. CO was purchased from Praxair and used as received.

**Synthesis of [<sup>Ph</sup>P<sub>2</sub>Cp]Li.** A solution of 1,1-C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>CH<sub>2</sub>-Cl)<sub>2</sub> (10 g, 36 mmol) in THF (120 mL) and toluene (20 mL) was heated to 65 °C and added dropwise to a solution of Ph<sub>2</sub>PLi (20.63 g, 107 mmol) in THF (120 mL) at 65 °C. The reaction mixture was allowed to cool to room temperature, and the solvent and excess Ph<sub>2</sub>PH were removed in vacuo. The white residue was then extracted with toluene and filtered through Celite. Removal of the solvent produced a yellow air- and moisture-sensitive oil (yield = 65%, 13.3 g). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\text{H}} = 0.05$  (s, 12H, Si(CH<sub>3</sub>)<sub>2</sub>); 1.30 (m, 4H, SiCH<sub>2</sub>P); 6.7 (m, 3H, C<sub>5</sub>H<sub>3</sub>); 7.00 (m, 20H, C<sub>6</sub>H<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}:  $\delta_{\text{P}} = -22.12$  (1:1:1:1 quartet,  $J_{\text{PLi}} = 84$  Hz).

**Synthesis of [<sup>i</sup>-PrP<sub>2</sub>Cp]ZrCl<sub>2</sub>, 2.** To an intimate mixture of Na/Hg (92 g, 0.012 mol) and [<sup>i</sup>-PrP<sub>2</sub>Cp]ZrCl<sub>3</sub> (1 g, 1.56 mmol) was added toluene (100 mL) under N<sub>2</sub>. The reaction mixture was degassed by three “freeze–pump–thaw” cycles and was stirred for 48 h under vacuum, during which the solution turned green. It then was filtered through Celite, and the solvent was evaporated under reduced pressure to yield a dark green microcrystalline solid (yield = 85%, 0.8 g). ESR (toluene):  $g = 1.96$ ;  $a(^{31}\text{P}) = 22.7$  G, 2P,  $a(^{91}\text{Zr}) = 13.6$  G, 1Zr. Anal. Calcd for C<sub>23</sub>H<sub>47</sub>Cl<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>Zr·(NaCl)<sub>0.1</sub>: C, 45.31; H, 7.77. Found: C, 45.13; H, 7.99. MS:  $m/e$  603 (M<sup>+</sup>).  $\mu$  (solid) = 2.0  $\mu_{\text{B}}$ ,  $\mu$  (solution in C<sub>6</sub>D<sub>6</sub>) = 1.8  $\mu_{\text{B}}$ .

**Synthesis of [<sup>i</sup>-PrP<sub>2</sub>Cp]ZrClMe, 3.** To a solution of [<sup>i</sup>-PrP<sub>2</sub>Cp]ZrCl<sub>2</sub> (0.25 g, 0.41 mmol) in toluene was added MeMgCl (0.32 mL, 0.45 mmol) dropwise at –78 °C. The solution was then warmed to room temperature and stirred for 4 h, during which a white precipitate formed. The reaction mixture was then concentrated under reduced pressure and filtered through Celite, and the solvent was evaporated, yielding a green powder (yield = 70%, 0.17 g). ESR (toluene):  $g = 2.01$ ;  $a(^{31}\text{P}) = 23.0$  G, 2P,  $a(^1\text{H}) = 8.0$  G, 3H,  $a(^{91}\text{Zr}) = 8.0$  G, 1Zr. Anal. Calcd for C<sub>24</sub>H<sub>50</sub>ClP<sub>2</sub>Si<sub>2</sub>Zr: C, 49.41; H, 8.64. Found: C, 49.33; H, 8.93.

**Reaction of [<sup>i</sup>-PrP<sub>2</sub>Cp]ZrCl<sub>2</sub>, 2, with CO; Formation of [<sup>i</sup>-PrP<sub>2</sub>Cp]Zr(CO)<sub>2</sub>Cl, 4.** A degassed solution of [<sup>i</sup>-PrP<sub>2</sub>Cp]ZrCl<sub>2</sub>, 2 (0.05 g, 0.09 mmol), in C<sub>6</sub>D<sub>6</sub> was stirred under 1 atm of CO for 24 h, during which the color changed from dark green to brown. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta_{\text{H}} = 0.12$  and 0.28 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.51 and 0.82 (dd, 2H, <sup>2</sup>J<sub>HH} = 15 Hz, <sup>2</sup>J<sub>PH} = 9 Hz, SiCH<sub>2</sub>P), 0.97, 1.22, 1.29, 1.32 (dd, 6H, <sup>3</sup>J<sub>HH} = 7 Hz, <sup>3</sup>J<sub>PH} = 7 Hz, CH-(CH<sub>3</sub>)<sub>2</sub>), 1.95 and 2.48 (sept, 2H, <sup>3</sup>J<sub>HH} = 7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 5.19</sub></sub></sub></sub></sub>

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Table 9: Crystallographic Data

|  | [ <sup>i</sup> -PrP <sub>2</sub> Cp]NbCl <sub>2</sub> (CO) ( <b>7</b> )           | [PhP <sub>2</sub> Cp]NbCl <sub>2</sub> (CO) ( <b>8</b> )                          | [ <sup>i</sup> -PrP <sub>2</sub> Cp]NbCl <sub>3</sub> ( <b>10</b> )              | [ <sup>i</sup> -PrP <sub>2</sub> Cp]MoCl <sub>2</sub> ( <b>11</b> )              |
|--|---|---|--|--|
| formula                                      | C <sub>24</sub> H <sub>47</sub> Cl <sub>2</sub> NbOP <sub>2</sub> Si <sub>2</sub> | C <sub>36</sub> H <sub>39</sub> Cl <sub>2</sub> NbOP <sub>2</sub> Si <sub>2</sub> | C <sub>23</sub> H <sub>47</sub> Cl <sub>3</sub> NbP <sub>2</sub> Si <sub>2</sub> | C <sub>23</sub> H <sub>47</sub> Cl <sub>2</sub> MoP <sub>2</sub> Si <sub>2</sub> |
| fw   | 663.57  | 769.63  | 641.01   | 608.59   |
| color, habit                                 | orange, prism   | red, irregular  | dark, prism  | dark brown, irregular  |
| cryst syst                                   | monoclinic  | orthorhombic  | monoclinic   | monoclinic   |
| space group                                  | <i>P2</i> <sub>1</sub> / <i>c</i>   | <i>Pca</i> 2 <sub>1</sub>   | <i>P2</i> <sub>1</sub> / <i>n</i>  | <i>P2</i> <sub>1</sub> / <i>a</i>  |
| <i>a</i> , Å                                 | 12.718(2)   | 28.5375(4)  | 17.0192(14)  | 15.4113(12)  |
| <i>b</i> , Å                                 | 16.609(3)   | 9.6009(8)   | 11.6262(13)  | 9.4576(12)   |
| <i>c</i> , Å                                 | 14.739(8)   | 13.1317(3)  | 17.0176(3)   | 20.4912(5)   |
| α, deg                                       | 90  | 90  | 90   | 90   |
| β, deg                                       | 101.6445(6)   | 90  | 116.4187(5)  | 104.3124(5)  |
| γ, deg                                       | 90  | 90  | 90   | 90   |
| <i>V</i> , Å <sup>3</sup>                    | 3049.3(5)   | 3597.9(3)   | 3015.6(3)  | 2894.0(3)  |
| <i>Z</i>                                     | 4   | 4   | 4  | 4  |
| <i>T</i> , °C                                | -93   | -93   | -93  | -93  |
| <i>D</i> <sub>calc</sub> , g/cm <sup>3</sup> | 1.380   | 1.421   | 1.412  | 1.397  |
| <i>F</i> <sub>000</sub>                      | 1328.00   | 1584.00   | 1340.00  | 1276.00  |
| radiation                                    | Mo  | Mo  | Mo   | Mo   |
| λ, Å   | 0.71069   | 0.71069   | 0.71069  | 0.71069  |
| μ, cm <sup>-1</sup>                          | 7.69  | 6.66  | 8.61   | 8.41   |
| correction factors                           | 0.5670-1.0015   | 0.6362-1.0000   | 0.7064-1.0082  | 0.8883-1.0000  |
| 2θ <sub>maz</sub> , deg                      | 60.1  | 60.1  | 60.1   | 60.1   |
| total no. of reflns                          | 28614   | 32169   | 28555  | 23795  |
| no. of unique reflns                         | 7291  | 5537  | 7744   | 7130   |
| <i>R</i> <sub>int</sub>                      | 0.030   | 0.045   | 0.052  | 0.027  |
| no. with <i>I</i> > 3σ( <i>I</i> )           | 5389  | 5988  | 6092   | 4661   |
| no. of variables                             | 289   | 396   | 280  | 271  |
| <i>R</i> <sup>a</sup>                        | 0.075   | 0.065   | 0.062  | 0.060  |
| <i>R</i> <sub>w</sub> <sup>a</sup>           | 0.089   | 0.054   | 0.111  | 0.064  |
| gof  | 2.53  | 1.38  | 1.19   | 1.36   |
| max Δ/σ                                      | 0.016   | 0.0003  | 0.001  | 0.001  |
| residual density, e/Å <sup>3</sup>           | -1.64-1.73  | -2.17-2.47  | -3.31-3.39   | -0.97-1.03   |

$$^a R = \sum |F_o| - |F_c| / \sum |F_o|; R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}.$$

(s, 2H, Cp), 5.21 (s, 1H, Cp). <sup>31</sup>P{<sup>1</sup>H}: δ<sub>P</sub> = 31.6 (s). IR (benzene, cm<sup>-1</sup>): 1888 (s, CO), 1978 (s, CO).

**Synthesis of [<sup>R</sup>P<sub>2</sub>Cp]NbCl<sub>2</sub>, R = *i*-Pr, Ph, 5, 6.** To a slurry of NbCl<sub>3</sub>(DME) (1 g, 3.89 mmol) in toluene (20 mL) was added the solution of [<sup>R</sup>P<sub>2</sub>Cp]Li (3.89 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred for 4 h, during which the solution turned brown-red. It was then filtered through Celite, and the solvent was evaporated under reduced pressure to produce a cherry-red microcrystalline solid (yield = 80%).

**For 5:** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ<sub>H</sub> = 0.00 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.28 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.50 (br s, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); 0.51 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 16 Hz, PCH<sub>2</sub>Si); 0.65 (dd, 2H, PCH<sub>2</sub>Si); 0.91 (br s, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); 1.33 (d, *J*<sub>PH</sub> = 7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); 1.63 (d, *J*<sub>PH</sub> = 7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>); 2.90 (sept, 4H, <sup>3</sup>J<sub>HH</sub> = 6 Hz, CHMe); 4.70 (s, 1H, C<sub>5</sub>H<sub>3</sub>); 5.60 (s, 2H, C<sub>5</sub>H<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: δ<sub>P</sub> = 24.62 (br s). Anal. Calcd for C<sub>23</sub>H<sub>47</sub>Cl<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>Nb: C, 45.62; H, 7.82. Found: C, 45.52; H, 7.73. MS: *m/e* 604 (M<sup>+</sup>).

**For 6:** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ<sub>H</sub> = -0.10 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.04 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.80 (ABX, 2H, SiCH<sub>2</sub>P); 1.30 (ABX, 2H, SiCH<sub>2</sub>P); 5.20 (s, 2H, C<sub>5</sub>H<sub>3</sub>); 5.80 (s, 1H, C<sub>5</sub>H<sub>3</sub>); 6.95 (m, 8H, Ph); 7.2 (m, 8H, Ph); 7.80 (m, 2H, *p*-Ph); 7.95 (m, 2H, *p*-Ph). <sup>31</sup>P{<sup>1</sup>H}: δ<sub>P</sub> = 22.50 (br s). Anal. Calcd for C<sub>35</sub>H<sub>39</sub>Cl<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>Nb(C<sub>7</sub>H<sub>8</sub>)<sub>0.75</sub>: C, 59.63; H, 5.59. Found: C, 59.84; H, 5.60.

**Synthesis of [<sup>R</sup>P<sub>2</sub>Cp]NbCl<sub>2</sub>(CO), R = *i*-Pr, Ph, 7, 8.** A degassed solution of [<sup>R</sup>P<sub>2</sub>Cp]NbCl<sub>2</sub> (1 mmol) in toluene (20 mL) was stirred under 1 atm of CO for 24 h, during which the color changed from dark red to orange. The solvent was then removed under vacuum to yield an orange microcrystalline solid (yield = 80%). Crystals suitable for X-ray analysis were grown by slow evaporation from a saturated toluene solution.

**For 7:** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ<sub>H</sub> = -0.05 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.25 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.80 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 16 Hz, SiCH<sub>2</sub>P); 0.90 (dd, 2H, SiCH<sub>2</sub>P); 1.10 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); 1.30 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>); 2.60 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, CHMe); 3.30 (sept, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, CHMe) 4.40 (s, 2H, C<sub>5</sub>H<sub>3</sub>); 6.05 (s, 1H, C<sub>5</sub>H<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: δ<sub>P</sub> = 25.66 (br s). Anal. Calcd for C<sub>24</sub>H<sub>47</sub>Cl<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>NbO: C, 45.50; H, 7.48. Found: C, 45.02; H, 7.29. IR (toluene, cm<sup>-1</sup>): 1914 (s, CO).

**For 8:** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ<sub>H</sub> = 0.02 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.25 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); 0.9 (dd, 2H, <sup>3</sup>J<sub>HH</sub> = 14 Hz, SiCH<sub>2</sub>P); 1.20 (dd, 2H, SiCH<sub>2</sub>P); 4.60 (s, 2H, C<sub>5</sub>H<sub>3</sub>); 6.40 (s, 1H, C<sub>5</sub>H<sub>3</sub>); 7.0 (m, 16H, Ph); 7.60 (m, 2H, *p*-Ph); 8.20 (m, 2H, *p*-Ph). <sup>31</sup>P{<sup>1</sup>H}: δ<sub>P</sub> = 18.19 (br s). Anal. Calcd for C<sub>36</sub>H<sub>39</sub>Cl<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>NbO: C, 56.18; H, 5.11. Found: C, 56.48; H, 5.14. IR (toluene, cm<sup>-1</sup>): 1927 (s, CO).

**Synthesis of [<sup>R</sup>P<sub>2</sub>Cp]NbCl<sub>3</sub>, 9, 10.** A solution of [<sup>R</sup>P<sub>2</sub>Cp]-Li (0.64 mmol) in toluene (5 mL) was added dropwise to a slurry of Nb(O)Cl<sub>3</sub>(THF)<sub>2</sub> (0.25 g, 0.7 mmol) in toluene (10 mL) at -40 °C. The color changed from yellow to green immediately. The reaction mixture was allowed to warm to room temperature and stirred for 10 h. It then was filtered through Celite and the solvent evaporated under reduced pressure to produce a green microcrystalline solid (yield = 60%).

**For 9:** Dark green crystals suitable for X-ray analysis were grown from slow evaporation of the toluene solution. ESR (toluene): *g* = 2.35, *a*(<sup>31</sup>P) = 26 G, 2P, *a*(<sup>93</sup>Nb) = 124 G, 1Nb. Anal. Calcd for C<sub>23</sub>H<sub>47</sub>Cl<sub>3</sub>P<sub>2</sub>Si<sub>2</sub>Nb: C, 43.10; H, 7.39. Found: C, 43.42; H, 7.51.

**For 10:** ESR (toluene): *g* = 2.04, *a*(<sup>31</sup>P) = 21 G, 2P, *a*(<sup>93</sup>Nb) = 117 G, 1Nb.

**Reaction of [<sup>i</sup>-PrP<sub>2</sub>Cp]NbCl<sub>2</sub> with PbCl<sub>2</sub>.** To a solution of [<sup>i</sup>-PrP<sub>2</sub>Cp]NbCl<sub>2</sub> (0.1 g, 0.17 mmol) in toluene (5 mL) cooled to -40 °C was added PbCl<sub>2</sub> (0.14 g, 0.51 mmol) in solid form. The reaction mixture was warmed to room temperature and stirred for 5 h, during which most of the PbCl<sub>2</sub> slurry was dissolved and the color changed from red to green. Filtration through Celite and evaporation of the solvent yield a yellow-green solid which gave ESR signals identical to [<sup>i</sup>-PrP<sub>2</sub>Cp]NbCl<sub>3</sub>.

**Synthesis of [<sup>R</sup>P<sub>2</sub>Cp]MoCl<sub>2</sub>, R = *i*-Pr, Ph, 11, 12.** To a slurry of MoCl<sub>3</sub>(THF)<sub>3</sub> (1 g, 2.39 mmol) in toluene (30 mL) was added the solution of [<sup>R</sup>P<sub>2</sub>Cp]Li (2.39 mmol) in toluene (10 mL). The reaction flask was covered with aluminum foil and heated to 65 °C for 24 h, during which the color slowly changed from orange to brown. After the reaction mixture cooled to room temperature, it was filtered through Celite and the solvent evaporated to yield a brown microcrystalline solid (yield = 85% and 65% for **11** and **12**, respectively).



For **11**: Brown crystals suitable for X-ray analysis were grown from slow evaporation of the toluene solution. ESR (toluene):  $g = 1.97$ ,  $a(^{31}\text{P}) = 15.2$  G, 2P,  $a(^{95}\text{Mo}) = 39.1$  G, 1Mo,  $a(^{97}\text{Mo}) = 23$  G, 1Mo. Anal. Calcd for  $\text{C}_{23}\text{H}_{49}\text{Cl}_2\text{P}_2\text{Si}_2\text{Mo}$ : C, 45.24; H, 8.09. Found: C, 45.54; H, 7.93.  $\mu(\text{solid}) = 1.98 \mu_{\text{B}}$ .

For **12**: ESR (toluene):  $g = 1.98$ ,  $a(^{31}\text{P}) = 11$  G, 2P,  $a(^{95}\text{Mo}) = 43.4$  G, 1Mo,  $a(^{97}\text{Mo}) = 23$  G, 1Mo. Anal. Calcd for  $\text{C}_{35}\text{H}_{39}\text{Cl}_2\text{P}_2\text{Si}_2\text{Mo}$ : C, 56.45; H, 5.28. Found: C, 56.92; H, 5.40.  $\mu(\text{solid}) = 2.10 \mu_{\text{B}}$ .

**X-ray Crystallographic Analyses of  $\{\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{-CH}_2\text{P-}i\text{-Pr}_2)_2\}\text{NbCl}_2(\text{CO})$  (**7**),  $\{\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{CH}_2\text{PPh}_2)_2\}\text{NbCl}_2(\text{CO})$  (**8**),  $\{\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{CH}_2\text{P-}i\text{-Pr}_2)_2\}\text{NbCl}_3$  (**9**), and  $\{\eta^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_2\text{CH}_2\text{P-}i\text{-Pr}_2)_2\}\text{MoCl}_2$  (**11**).** Crystallographic data were collected on a Rigaku/ADSC CCD diffractometer and appear in Table 9. The final unit cell parameters were obtained by least squares on the setting angles for 28614 reflections (**7**), 32169 reflections (**8**), 28555 reflections (**9**), and 23795 reflections (**11**) with  $2\theta = 4.0\text{--}60.1^\circ$ . The data were processed<sup>53</sup> and corrected by Lorentz and polarization effects and absorption (empirical: based on a three-dimensional analysis of a symmetry-equivalent data).

The structures were solved by heavy-atom Patterson methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions with C–H = 0.98 Å and  $B_{\text{H}} = 1.2_{\text{bonded atom}}$ . Unmodi-

fied statistical weights ( $w = 1/\sigma^2(F_o)^2$ ) were employed for all four structures. Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.<sup>54,55</sup>

Selected bond lengths and bond angles appear in Tables 1–8. Tables of final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

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**Supporting Information Available:** Tables of final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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